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PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Improvements in or relating to fibre reinforced polyamides

- We, CHEMISCHE WERKE WITTEN, GESELLSCHAFT MIT BESCHRANKTER HAFTUNG, a German body corporate of Witten/Ruhr, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- 10 This invention is concerned with improvements in or relating to fibre reinforced polyamides, in particular to polyamides reinforced by inorganic fibres and a process for producing said reinforced polyamides.
- 15 It has been proposed to improve the mechanical properties of polyamides by incorporating short glass fibres or asbestos fibres therein. Polyamides having useful properties can be obtained by incorporating up to 40% by weight of such inorganic fibres into the polyamide.
- 20 In previously proposed condensation processes the polyamides were obtained as viscous melts into which it was difficult to distribute fibrous materials since the fibres tend to felt together and form hard masses. Two ways of overcoming this difficulty have been proposed. In the first method continuous skeins of the fibre material are pulled through the synthetic resin melt and the coated skeins are then chopped to yield a granulate. Due to the better workability of the fibre reinforced polyamides, however, it is preferred to use short fibres of from 25 1 to 4×10^{-2} cm in length. In this case the fibres are usually incorporated in the polyamide by vigorous mixing with the polymer at room temperature the polymer being as finely divided as possible, and then homogenising the resulting mixture in the molten state in a screw extruder or a kneader.
- Since short glass fibres tend to felt into small balls, it is very difficult to distribute them by means of a dry mixing procedure or a dry stirring operation, even in the presence of a second material, such as a polyamide powder or granulate. In addition the glass fibres are partly broken up. A subsequent homogenisation of the polyamide melt involves an additional thermal strain on the polymer, and furthermore a double mixing process is expensive.
- 50 We have now derived a process whereby fibre reinforced polyamides in discrete particle form can be obtained directly without the need for a subsequent granulating or mixing operation.
- According to the present invention there is provided a process for the production of a polyamide composition in discrete particle form which comprises uniformly distributing inorganic fibres in an "inert solvent," as herein defined, and subsequently reacting a diaryl ester of a dicarboxylic acid with a diamine in said inert solvent to form discrete particles comprising polyamide particles rigidly connected to said inorganic fibre. The resulting discrete particles are generally obtained in the form of a powder having a particle size of up to the order of 500 microns.
- 75 The polyamide condensation process employed must be such as to provide the polyamide in discrete particle form. It is thus essential that the inert solvent used be one which is a non-solvent for the polyamide produced although it must dissolve the acid (or ester) and amine starting materials for

the polyamide. Depending on the temperature used during the condensation it may be necessary to exchange the inert solvent initially used to form the fibre suspension for a second higher boiling inert solvent during the condensation.

The inorganic fibres used are preferably glass fibres or asbestos fibres, the former yielding a finely powdered product and the latter a slightly flocculent product; both products being suitable for processing on synthetic resin processing machine or for use as moulding materials. The glass fibres are preferably made from a non-reacting glass. The fibres used preferably have an average diameter of from 1×10^{-4} on to 2×10^{-3} cm and preferably have an average length of from 5×10^{-3} to 1×10^{-1} cm.

The polyamide condensation reaction may be effected as described in Patent Specifications Nos. 1,021,608 and 1,100,357, the former relating to aromatic dicarboxylic acids (isophthalic and terephthalic acid) and the latter relating to aliphatic and cycloaliphatic acids. In both prior Specifications primary aliphatic or araliphatic diamines are employed. In the process of the present invention it is preferred to use diphenyl esters of the acid.

Observation of the mixture obtained under a microscope shows that the polyamide particles mostly adhere directly to the fibres, in contrast to the situation where a mixture of a preformed polyamide powder with short glass fibres has been obtained by stirring in a suspension medium, such as water or methanol, where a loose juxtaposition of polyamide particles and fibres is observed. By pre-treatment of the fibres with a sizing agent, such as for example a silane, the adhesion of the polyamide particles to the fibre surface can be further improved. Subsequent separation of polyamide and filler does not take place.

The particle size of the polyamide powder used can be varied by selection of the inert solvent for the precondensation. It has been found that the finest powders are obtained when using benzene; that highly agglomerated particles are obtained when using dialkyl benzenes; and that powders of intermediate size are obtained by suitable mixtures of solvents.

Where asbestos fibres are used a slightly larger quantity of solvent or dispersing agent is necessary as compared with the amount needed in the preparation of un-reinforced polyamide powders. When using glass fibres having a length of up to 1×10^{-1} cm no additional quantities of solvents are necessary.

The quantity of fibres which can be mixed with a polyamide prepared according to the above described condensation process is not particularly critical. When moulding poly-

amides, e.g. on injection moulding machines, a proportion of from 10 to 40 per cent by weight of fibres, calculated on the total weight of the starting materials has been found to be preferred.

Apart from the short inorganic fibres, the polyamides can contain further additives, such as dyestuffs, stabilisers, lubricants or pigments.

The invention will now be illustrated with reference to the following Examples.

Example 1

Polyhexamethylene isophthalamide/terephthalamide (70/30) containing 33% of glass fibres

In a 2 litre round bottomed flask fitted with a stirrer, thermometer, dropping funnel and a fractionating column 61.5 g. of unsized glass wool with a filament diameter of 1×10^{-3} cm and an average filament length of 2×10^{-2} cm are distributed in 1000 ml. of benzene using good stirring with a standard glass paddle stirrer. In order to remove moisture which may be present 50 ml. of benzene are distilled off. The glass fibre is uniformly distributed, without felting.

159 g. of a mixture of 70% of diphenyl isophthalate and 30% of diphenylterephthalate (0.5 mol) are then completely dissolved in the warm benzene and then a solution of 58 g. of hexamethylene diamine (0.5 mol) in 100 ml. of benzene is added dropwise over 10 minutes with vigorous stirring at 80°C and stirring is then continued for 1 further hour. The benzene is then distilled off up a small column and diethyl benzene added at the distillation rate of the benzene until the internal temperature has risen to 170°C . At this temperature the reaction mixture is aftercondensed for 3 further hours and during this time phenol is slowly distilled off azeotropically with a proportion of the diethyl benzene.

After cooling, the reaction product is vigorously filtered with suction, washed with methanol, and then dried in vacuo.

A free-flowing powder is obtained in which it is difficult to distinguish the glass fibres with the naked eye. Under the microscope it can be seen that a large proportion of the spherical polyamide particles are adhering to the glass fibres.

In order to ascertain the uniformity of distribution throughout the material 6 samples of 10 g. each were taken at different places from a large batch, and completely extracted with phenol/methanol. The weight of the residual glass fibre was determined. A maximum difference of 1% was found.

Determination of the specific viscosity number was effected by weighing out 1.492 g. of the mixture and dissolving it in 100 ml. of a mixture of phenol and tetra-

chloroethane (60/40). The residual glass fibre was filtered off and the measurement carried out on the filtrate. Specific viscosity number=3.09.

5 **Example 2**
Polyhexamethylene isophthalamide/
terephthalamide (70/30) with 30% of glass
fibre

10 Using the general method described in Example 1, 52.7 g. of short glass fibres with a filament diameter of 1×10^{-3} cm and an average filament length of 8×10^{-2} cm and
15 provided with a silane sizing agent, were uniformly distributed using vigorous stirring in a mixture of 500 ml. of benzene, and 500 ml. of diethyl benzene, 0.5 mol of the diphenyl ester mixture with hexa-
20 methylene diamine was precondensed at 90°C and then aftercondensed at 170°C , during which time 500 ml. diethyl benzene was added to replace the benzene distilled off. The isolation of the solid mixture was
25 effected as described in Example 1.

The viscosity number was 2.71. Using a microscope it could be seen that the adhesion on the glass fibre had been markedly improved; the particles of the polyamide
30 were larger than those in Example 1.

Example 3
Polyhexamethylene adipamide with 30% of
glass fibres

35 52.7 g. of short glass fibres were suspended in 1000 ml. of dodecyl benzene. Then 149 g. of diphenyl adipate (0.5 mol) were dissolved at 80°C and subsequently
40 reacted with a solution of 58 g. of hexamethylene diamine in 100 ml. of dodecyl benzene at 90°C . The temperature was raised after one hour to 90°C and the reaction mixture after-condensed for a further
45 three hours, during which time the liberated phenol slowly distilled off. A homogeneous powdery mixture was obtained which was isolated, as described in Example 1, and
50 washed with benzene. The specific viscosity number was 1.7.

Example 4
Polyhexamethylene isophthalamide/
terephthalamide (70/30) with 20% of
55 asbestos fibres

27.4 g. of asbestos fibre — 7D were suspended in 1200 ml. of diethyl benzene using
vigorous stirring. A large-area paddle stirrer
60 was used. 0.5 mol of the diphenyl ester mixture with hexamethylene diamine were precondensed in this suspension and after-condensed at 180°C as described in Example 1. The isolation of the solid mixture was
65 effected as described in Example 1. A flocculent voluminous material was obtained.

The specific viscosity number was 2.32.

Our copending Application No. 24492/66 (Serial No. 1,147,053) describes and claims a process for the incorporation of finely
70 divided fillers, such as inorganic or synthetic resin powders, into polyamides using a process otherwise similar to that of the present invention.

WHAT WE CLAIM IS:—

1. A process for the production of a polyamide composition in discrete particle form which comprises uniformly distributing inorganic fibres in an "inert solvent," as
80 herein defined, and subsequently reacting a diaryl ester of a dicarboxylic acid with a diamine in said inert solvent, to form discrete particles comprising polyamide particles rigidly connected to said inorganic fibre.
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2. A process as claimed in claim 1 wherein the fibres are glass fibres or asbestos fibres.

3. A process as claimed in claim 1 or claim 2 wherein the fibres used have an
90 average diameter of from 1×10^{-4} cm to 2×10^{-3} cm.

4. A process as claimed in any one of the preceding claims wherein the fibres used have an average length of from 5×10^{-3} cm
95 to 1×10^{-1} cm.

5. A process as claimed in any one of the preceding claims wherein the fibre reinforced polyamide contains from 10 to 40%
100 by weight of the fibres.

6. A process as claimed in any one of the preceding claims wherein the polyamide is a polyamide of isophthalic acid and/or
105 terephthalic acid and a primary aliphatic diamine.

7. A process as claimed in claim 6 wherein the polyamide is derived from a diphenyl ester of said acid.

8. A process as claimed in claim 6 or claim 7 wherein the polyamide condensation
110 reaction is carried out as described and claimed in Patent Specification No. 1,021,608.

9. A process as claimed in any one of claims 1 to 5 wherein the polyamide is a
115 polyamide of an aliphatic or cycloaliphatic dicarboxylic acid and a primary aliphatic diamine.

10. A process as claimed in claim 9 wherein the polyamide is derived using a
120 diphenyl ester of said acid.

11. A process as claimed in claim 9 or claim 10 wherein the polyamide condensation reaction is carried out as described and
125 claimed in Patent Specification No. 1,100,375.

12. A process as claimed in claim 1 substantially as herein described.

13. A process for the production of a

fibre reinforced polyamide in discrete particle form substantially as herein described with reference to the foregoing Examples.

14. Fibre reinforced polyamides whenever
5 produced by a process as claimed in any one of the preceding claims.

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